

MINERAL LIBERATION OF ILLINOIS COALS

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INTRODUCTION

Extensive studies of coal structure and utilization have been conducted on every known aspect of coal for many decades in an attempt to produce a more efficient and less polluting energy source. The first priority toward this energy goal is to deep clean coal prior to combustion, gasification, or liquefaction. Deep cleaning coal requires the liberation of pyrite and other minerals to facilitate high recovery of clean product. High recovery is necessary to make any cleaning process economically feasible. The high degree of liberation necessary for deep cleaning suggests that the physical properties of coal/mineral interaction be considered during comminution. Most grinding techniques use random fracture to reduce coal to roughly a cubic or spherical shape which simplifies the prediction of combustion rates in various types of furnaces[1]. This type of grinding does not significantly aid in exposing minerals for possible liberation. In particular, current grinding processes have never been able to effectively liberate microcrystalline pyrite from coal. Studies have shown that 60 to 80% of the mineral content in coal is located in the bedding planes[2]. These interfacial areas, separating relatively clean coal bands, are zones of weakness which contain porosity, fractures, and poorly bonded minerals[2][3].

This paper is a summary of research efforts to utilize bedding plane interfacial areas as a means to improve liberation of pyrite and other minerals in the final product. By cleaving large coal particles along the interfacial boundaries, relatively clean coal particles would be produced that have the majority of the mineral matter coating the exterior of each particle. Subsequent grinding would attrite the outer surface into ultrafine size distributions that allow separation of minerals and macerals particles. These particles would then be separated from the clean coal by sieving.

Over the past few years, low temperature studies have been conducted to determine the relationships between the fracture resistance of coal treated at low temperature and the effectiveness of coal grinding, to investigate the effect of cryogenic temperature treatment on the effectiveness of coal grinding and potential of selective pyrite liberation[4][5]. This work indicated that brittleness after rewarming increases with decreasing cryogenic treatment temperature. Experimental data has shown that the effect of cryogenic temperature does increase friability, mean particle size is significantly reduced, and pyrite/mineral liberation increased. This was the result of increased crack propagation and decreased microhardness[6][7]. Several methods of preconditioning are currently being investigated; thermal, mechanical, and chemical.

In thermal treatments, coals are being exposed to cyclic freezing and thawing at equilibrium moisture contents. The freeze/thaw cycling is based on using the expansion property of freezing water to place pressure on fracture ends in the hope to expand and propagate cracking with the particle. In mechanical preconditioning, literature indicates that roll crushing yields particles that are plate-like or flakes and have a high aspect ratio[1][8]. Roll crushing and stage roll crushing of raw and cryogenic samples were examined to determine if this mechanical step would enhance liberation in subsequent ball milling. Solvent swelling of coal during mild extraction has been examined as a preconditioner. The reason is to enlarge pores during extraction and remove the soluble organic. The organic soluble phase may be responsible for the thermoplastic matrix of coal and reduced mineral liberation rates.

EXPERIMENTAL

The main coal used in this research is Illinois Basin Herrin #6 coal. This is due to its local economic importance and unique microdispersed pyrite particles. These microdispersed pyrite particles are the most difficult to liberate and separate of all the Illinois Basin coals. Wyodak and Pittsburgh coal is also currently being tested.

Knoop microhardness testing after rewarming was employed to examine brittleness of coal and the effect of cryogenic temperature on its microhardness[1][6][7]. An Automated Image Analyzer connected with an optical microscope was used to obtain pyrite liberation and particle size distributions for samples ground by a Fritsch centrifugal ball mill. Surface artifacts were examined by scanning electron microscopy (SEM) and optical microscopy.

The desired cryogenic temperatures were obtained using liquid nitrogen as a refrigerant to cool a flowing gaseous nitrogen stream which was in actual contact with the specimen. Detailed experimental setup and procedures for cryogenic treatment are given elsewhere[5][6].

Using the thermal expansion of water when frozen, coal samples were mixed with various weight percents of distilled water; 5, 10, and 20 grams. The samples were sealed into plastic freezer bags with all excess air removed. These samples were frozen and thawed for various cycles that range from 5 to 20 times.

Mechanical preconditioning of the coal was conducted using a roll crusher with its rollers set at staging widths of various increments; 0.1", 0.7", 0.5", and 0.3". Untreated and cryogenic coal samples were used in these experiments.

An evaluation of THF extraction as a means of preconditioning the unextractable residue is currently being conducted.

RESULTS AND DISCUSSION

Figure 1 includes information on three coals; Herrin Illinois #6, Wyodak, and Pittsburgh. Data from these samples of untreated and cryogenically treated coals are included. Rate of particle size reduction is greater for cryogenic coals. For a given grinding time, pyrite liberation is greater for cryogenically treated coals, but this is obtained by reduced particle size and not by enhanced selective liberation. The untreated coals give similar shape curves. The slope of liberation changes during treatment. During initial particle size reduction, the liberation is slow. When particle size distribution reaches 70 to 100 μm , a jump in liberation occurs. This is followed by a period in which coal becomes fine in size but liberation remains static. For the cryogenically treated coals, particle size reduction is faster and the initial slow period is not observed. A relatively high rate of liberation occurs as the mean particle size distribution is reduced from 90 to about 40 μm . The rate of liberation is relatively linear until the mean size approaches 10 to 12 μm and begins to level off as 100% liberation is approached. The earlier liberation is more selective for the untreated coals, but a maximum liberation level is observed. The liberation of cryogenically treated coals reaches a higher limit. Although the selectivity of untreated coals is higher, the extent of liberation is not sufficient to be of commercial interest. Even though the amount of pyrite and the particle size distribution of pyrite vary for the three untreated coals, the extent of liberation approaches the same limit ($\approx 84\%$) and the same mean particle size of 20 μm . The untreated Pittsburgh coal has a larger pyrite size distribution than the Illinois coal which results in a higher rate and selectivity of pyrite liberation as expected[6]. Thus cryogenic treatments are helpful in increasing the ultimate liberation. This is probably due to two factors. One is enhanced cracking around pyrite. The second is enhanced fracture, flaw generation, in the coal matrix[6]. This allows for the coal to be reduced in size as compared to untreated coals. Even with cryogenic treatments, ultrafine particle sizes must be obtained to reach sufficient levels for deep cleaned coal.

Economic considerations of cryogenic treatments makes it a less than desirable method for liberation. For this reason freeze/thaw cycling was studied as an alternative. Figure 2 is a comparison of pyrite liberation to the mean particle size for untreated, cryogenically treated, and freeze/thaw treated Illinois coal samples after ball milling. The points of each plot represent a grinding time, from left to right, of 1, 3, 5, 7, and 10 minutes. As discussed in figure 1, the rate of liberation for the untreated coal is slow until a mean size of about 70 μm is reached. A large jump in liberation occurs until a mean size of about 50 μm is reached. At that time the liberation becomes nearly stationary. Freeze/thaw liberation appears to be an extension of the untreated plot and increases to about 84%. Rapid particle mean size reduction is very evident with the freeze/thaw treatment. Three minutes of ball milling of freeze/thaw sample yields about the same size distribution as ten minutes ball milling of the untreated sample. Freeze/thaw

cycling improves the upper level of liberation compared to the untreated. However, cryogenic treatment yields 93% pyrite liberation while freeze/thaw yields 84%.

Figure 3 compares freeze/thaw, cryogenic roll crushed, untreated, and untreated roll crushed Illinois coal samples after subsequent ball milling for pyrite liberation at various mean particle sizes. The points of each plot represent a grinding time, from left to right, of 1, 3, 5, 7, and 10 minutes. All three plots show significantly improved liberation compared to the untreated sample. The BG-CRYO is cryogenically treated for five minutes, compared to 10 minutes in Figure 2, and staged crushed from 0.1" to 0.05". At five minute exposure time, the cryogenic liberation does not approach the level attained by freeze/thaw. This would indicate that freeze/thaw results are better than 5 minute cryogenic exposure but falls short of 10 minute cryogenic exposure results. The freeze/thaw sample, was thermally cycled 10 times with 10% by weight distilled water added. This sample shows a nearly linear increase in liberation to about 87%. It may be concluded that the mechanical and thermal treatment increases liberation above that attainable by untreated samples ball ground in an identical manner.

Figure 4 is a comparison of single roll crushing and staged roll crushing of untreated, UNT-RC-0.1, and cryogenically treated, cryo-, coal followed by ball milling. The slope for all the samples is nearly the same. The rate of pyrite liberation of the untreated single roll crush sample, UNT-RC-0.1 is consistently less than the other roll crushed samples but much greater than the rate of liberation for the ball milled only sample. Single roll crushing was conducted at 0.07" gap on one cryogenic sample still at liquid nitrogen temperature, CRYO-C-RC-0.07, and another allowed to rewarm before roll crushing, CRYO-R-RC-0.07. The rewarmed sample maintained a consistently higher liberation rate throughout. Roll crushing at 0.1", CRYO-R-RC-0.1, has better liberation than roll crushing at 0.07", CRYO-C-RC-0.07. This is possibly due more force being applied to the 0.07" sample to the extent that the pyrite particles are embedded into the viscoelastic coal matrix. Both the rewarmed staged, CRYO-R-SC and single roll crushed samples had better results than both the untreated and cold roll crushed samples. Crack propagation may be improved upon thermal expansion after thermal contraction. If the stage crushed sample was ball ground for 10 minutes and the slope of this sample remains consistent with the other samples, a higher level of pyrite liberation should be obtained.

CONCLUSIONS

This study of preconditioning treatments indicates that both thermal and mechanical methods will improve pyrite liberation above that obtained for untreated samples. Freeze/thaw cycling improves liberation but not to the degree obtained by cryogenic treatment. Rewarming of cryogenically treated coal prior to comminution improves the overall pyrite liberation. Stage roll

crushing improves liberation. Enhanced liberation of pyrite by all the preconditioning methods presented is at the expense of smaller mean particle sizes.

REFERENCES

1. Durney, T.E., and Moley, T.P., "Particle Shape Effects Due to Crushing Method and Size", International Journal of Mineral Processing, Vol. 16, pp109-123, 1986.
2. Stach, E., Textbook of Coal Petrology, Pub. Gebruder Borntraeger, Berlin and Stuttgart, Germany, 1982.
3. Ward, C.R., ed., Coal Geology and Coal Technology, Blackwell Scientific Publications, Ca., U.S.A., pp157, 1984.
4. Yen. S.C., and Hippo, E.J., "Comminution Employing Liquid Nitrogen Pretreatment", Final Report to PETC, August 31, 1991.
5. Yen. S.C., and Hippo, E.J., "Enhanced Coal Cleaning Through Low Temperature Treatment of Coal", Final Report to The Center for Research of Sulfur in Coal, August 30 1990.
6. Blankenship, M., M.S. Thesis, Southern Illinois University at Carbondale, Carbondale, Il., 1991.
7. Jao, H., M.S. Thesis, Southern Illinois University at Carbondale, Carbondale, Il., 1991.
8. Mishra, S.K., and Klimpel, R.R., Fine Coal Processing, Noyes Publications, Park Ridge, N.J., U.S.A., pp 19-37, 1987.

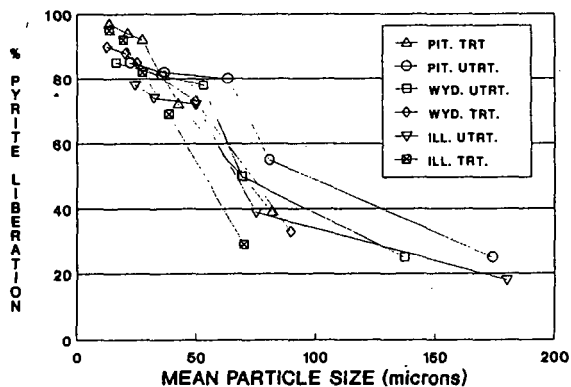


Figure 1. Comparison of Pyrite Liberation as a Function of Mean Particle Size for Pittsburgh, Wyodak, and Illinois No. 6 Coals. Both Cryogenically Treated and Untreated Samples Were Ball Milled for Various Times.

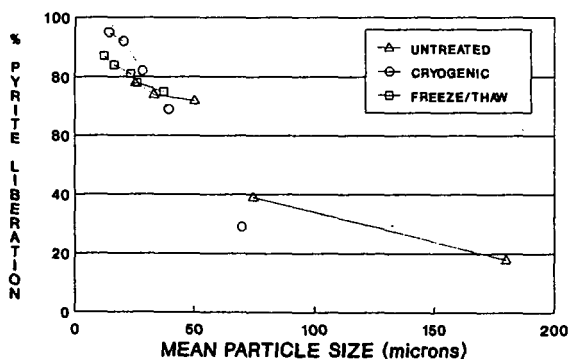


Figure 2. Comparison of Pyrite Liberation as a Function of Mean Particle Size for Illinois No. 6 Coals. Untreated, Cryogenic, and Freeze/Thaw Treatments Are Compared.

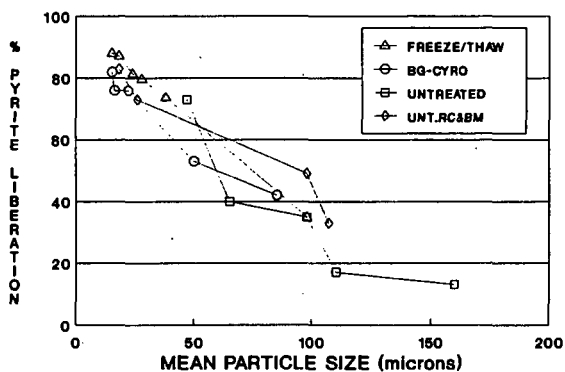


Figure 3. Comparison of Pyrite Liberation as a Function of Mean Particle Size for Illinois No. 6 Coals. Data Includes Roll Crushing, Freeze/Thaw, and Cryogenic Treatments.

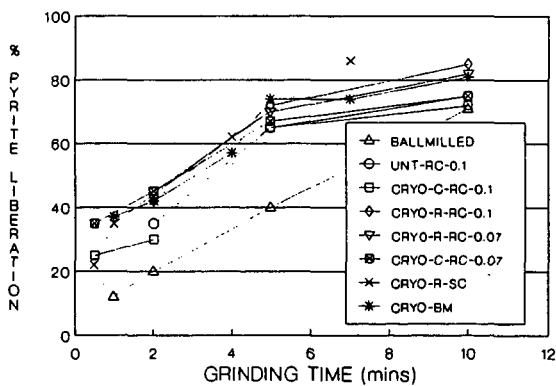


Figure 4. Pyrite Liberation as a Function of Grinding Time for Illinois No. 6 Coals with Various Mechanical and Thermal Pretreatments.